

3 LITERATURE SEARCH ON THE MANUFACTURE OF LAYERS OF MOLYBDENUM,  
TUNGSTEN, AND THENIUM BY THERMAL DECOMPOSITION OF THEIR  
CARBONYLS OR REDUCTION OF VOLATILE HALIDES 5

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LITERATURE SEARCH ON THE MANUFACTURE OF LAYERS OF MOLYBDENUM,  
TUNGSTEN, AND RHENIUM BY THERMAL DECOMPOSITION OF THEIR  
CARBONYLS OR REDUCTION OF VOLATILE HALIDES

M. Kadner

ABSTRACT. Pure coatings of Mo, W, or Re are advantageously deposited from the vapors of the fluorides (W, Re) or the chlorides (Mo, W, Re) by reduction with hydrogen.

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Details, conditions, and results are discussed.

Summary

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The research primarily covered the literature cited in "Chemical Abstracts" 56 (1962) to 60 (1964) under the heading "Coating(s)".

The following reference works were employed:

Hodgman, Handbook of Chemistry and Physics (Ref. 1)

Sidgwick, The Chemical Elements and their Compounds (Ref. 2)

Sherwood (Ref. 3) gives a general summary of "Chemical Vapor Deposition" methods.

The results of the research can be summarized as follows:

In order to manufacture layers of molybdenum, tungsten or rhenium or pure metals, carbonyls are thermally decomposed (Mo, W), or fluorides (W, Re) or chlorides (Mo, W, Re) are reduced with hydrogen. Apparently the carbonyls play a less important role in the manufacture of pure layers.

Molybdenum layers are usually manufactured by reduction of  $\text{MoCl}_5$ , which is vaporized at 200 to 280°C in an argon current, with hydrogen at 600 to 850°C. Furthermore, molybdenum is separated by thermal decomposition of  $\text{Mo(CO)}_6$  at 400 to 600°C in the presence of hydrogen and water vapor.

The purest tungsten layers are obtained by reduction of  $\text{WF}_6$  with hydrogen at 600 to 700°C and 20 to 760 Torr. The  $\text{H}_2$ - $\text{WF}_6$  ratio varies between 1:1 and 140:1. In addition, this is also done at very low pressures ( $10^{-3}$  Torr). Tungsten can also be separated by reduction of  $\text{WCl}_6$  with hydrogen or by the decomposition of a mixture of tungsten bromides, as well as by thermal decomposition of  $\text{W(CO)}_6$  at 200 to 600°C in the presence of hydrogen and water vapor.

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\* Numbers in the margin indicate pagination in the original foreign text.

There are relatively few studies regarding the separation of rhenium. It can be separated from  $\text{ReF}_6$  at temperatures from 400 to 800°C and pressures of 10 Torr in the presence of hydrogen. It is also possible to reduce  $\text{ReOCl}_4$  with hydrogen at 800 to 1300°C, which results in rhenium.

#### Molybdenum

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Density 10.2 g/cm<sup>3</sup>

Flow point 2622 ± 40°C

Condensation point 4864°C (at 3300°C ≈ 1 Torr)

Other properties are given in a publication by Schreiter (Ref. 4).

According to Braun (Ref. 5) molybdenum has recently also been introduced into metal technology, after new methods of manufacture and metal working were found. In addition to the manufacture of molybdenum powder, carried out on a large scale by the reduction of ammonium molybdate or of the oxide  $\text{MoO}_3$  with hydrogen, which leads to molybdenum with a purity of about 99.98%, the following methods are also used to manufacture molybdenum:

Thermal disassociation of  $\text{MoS}_2$  in a vacuum

Reduction of molybdenum chloride with magnesium

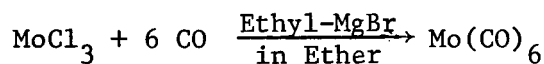
$\text{Mo(CO)}_6$  and  $\text{MoCl}_5$  are used as initial materials for the manufacture of molybdenum layers. Due to a general interest, we will discuss  $\text{MoF}_6$  below.

#### $\text{Mo(CO)}_6$

Condensation point 156°C; decomposition begins at 150°C.

Sublimates with hydrogen or carbon dioxide at 30 to 40°C.

Manufacture:



According to Lander (Ref. 6) molybdenum layers are manufactured by the thermal decomposition of  $\text{Mo(C)}_6$ , especially in the presence of hydrogen as the carrier gas. By changing the separation conditions, it is possible to vary the carbon content of the separated metal (molybdenum, also tungsten or chrome) between 0 and 35 atomic percent. The higher the gas pressure of the produced carbon monoxide and carbon dioxide, the larger it is, and the lower the separation temperature is. The carbon separation is essentially prevented for the following conditions:

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Separation Temperature in °C	Ratio H <sub>2</sub> :CO
400	6000 to 10000
500	3000
600	10000

At high temperatures and higher total pressures of H<sub>2</sub> + CO (for p > 1 Torr), the decomposition of the carbonyl already begins in the gas phase. Thus, a loose and unserviceable covering is created.

The rate of separation of the metal decreases with increasing temperature. Therefore, it is useful to work at 500 to 600°C and to force back the carbon separation by the addition of water vapor (regulation of the water-equilibrium) and which proceeds according to the reaction  $\text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O}$ . No oxides are produced neither here or in the presence of 0.5% air.

Pure molybdenum was separated at a temperature of 550°C and pressures of 0.7 Torr hydrogen as well as 0.04 Torr carbon monoxide and carbon dioxide. In order to achieve a good bond, it is advantageous to first clean the surface to be metallized with hydrogen.

It should be noted that pure tungsten is separated in a similar way, but /6 at much higher pressures (higher decomposition rates).

US-Patent 3,023,491 (Ref. 7) gives a method for the manufacture of coatings by the decomposition of molybdenum, tungsten and chrome carbonyls. The carbonyls are dissolved in dioxane as well as tetrahydrofurane, or vaporized with the solvent at 90 to 100°C and then decomposed above 150°C. In this case it is not necessary to work in a vacuum. By decomposition of Mo(CO)<sub>6</sub> at 315°C layers 0.2 to 0.3 mm/<sup>thick</sup>were manufactured. The working temperatures are in general 200 to 250°C. The method is supposed to be universally applicable.

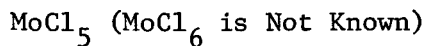


White crystals

Flow point 17.5°C, Condensation point 35°C

Manufacture from the elements.

This compound is not mentioned as the initial material for the manufacture of coatings in the literature reviewed by us (however, see tungsten).



Dark green to black crystals; the vapor is dark red.

Flow point 194°C, Condensation point 268°C

Manufacture from the elements.

According to Gadiyer (Ref. 8), layered uranium dioxide covered with layers /7 of molybdenum is manufactured by the reduction of  $\text{MoCl}_5$  with hydrogen at  $600^\circ\text{C}$ . The uranium dioxide particles are applied in layers for one hour at a hydrogen flow rate of 1:1 with the addition of argon in the ratio 100 ml/min in a fluidized bed, and layers 7 to 10 mm thick are obtained. The  $\text{MoCl}_5$  is vaporized at about  $200^\circ\text{C}$ ; the hydrogen is added later. The hydrogen chloride is collected in subsequent washing bottles.

Furthermore, the manufacture of  $\text{MoCl}_5$  and the metallographic properties of the coatings are discussed.

Badiali (Ref. 9) describes a method of manufacturing extremely pure molybdenum by the reduction of  $\text{MoCl}_5$  in a hydrogen-argon current at  $850^\circ\text{C}$  and 5 to 20 Torr (optimum condition). The ratio  $\text{Ar:H}_2$  was 2.3:31 (1/h). The  $\text{MoCl}_5$  is vaporized at  $280^\circ\text{C}$  and carried along with the argon current, and hydrogen is added later. The method can also be used at normal pressure. The analysis of the separated metal resulted in:

C	89 ppm
H	3 ppm
N	9 ppm
O	650 ppm

Lamprey (Ref. 10) describes a similar procedure, but no coatings are manufactured (see  $\text{WCl}_6$ ).

US-Patent 3,089,785 (Ref. 11) also states that in addition to the chlorides of tantalum, niobium, tungsten, zirconium and titanium, molybdenum chloride can also be used for the manufacture of coatings by reduction with hydrogen.

#### Tungsten

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Density  $19.3 \text{ g/cm}^3$

Flow point  $3370^\circ\text{C}$

Condensation point  $5900^\circ\text{C}$  ( $6700^\circ\text{C}$ )

The compounds  $\text{W(CO)}_6$ ,  $\text{WF}_6$ ,  $\text{WCl}_6$  and  $\text{WBr}_6$  were used for the manufacture of tungsten layers.

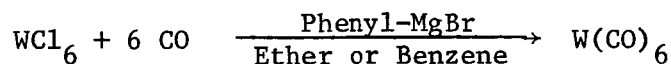
#### $\text{W(CO)}_6$

Colorless crystals

Condensation point  $175^\circ\text{C}$ ; sublimes after  $50^\circ\text{C}$

The decomposition begins at  $150^\circ\text{C}$

Manufacture:



According to McGuire (Ref. 12) coatings of tungsten are manufactured by the decomposition of  $\text{W(CO)}_6$  at 200 to 600°C in the presence of hydrogen or water vapor. Due to the additives, the carbon and carbide content can be held small. At high temperatures, the carbon content and the separation rates decrease.

Lander (Ref. 6) and Breining (Ref. 7) used  $\text{W(CO)}_6$  as the initial material for the separation of tungsten (see  $\text{Mo(CO)}_6$ ).

Finally, we should also mention a study (Ref. 13) on molybdenum, niobium and Mo-Nb-alloys.



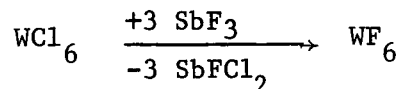
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Flow point 2.5°C at 375 Torr

Condensation point 19.5°C at 760 Torr

Reacts with all metals, except gold and platinum

Manufacture: from the elements or:



According to Nieberlein (Ref. 14) tungsten of the highest purity (99.99%) is manufactured by the reduction of  $\text{WF}_6$  with hydrogen at 600°C. The most important impurities (more than 10 ppm) were silicon (28 ppm) and carbon (15 ppm). The density of the separated tungsten was 19.25 g/cm<sup>3</sup>. In addition to teflon and Kel-f (for the flowmeter), which is a polymer flourine hydrocarbon, they used copper, Monel and Inconel. The hydrofluoric acid formed was collected with saturated boric acid solution.

According to Oxley (Ref. 15), very pure tungsten is also separated from  $\text{WF}_6$  in the presence of hydrogen and nitrogen. The content of foreign materials is less than 100 ppm, of which 20 to 50 ppm are fluorine. The author gives an equation to calculate the reaction rate above 300°C.

Nyce (Ref. 16) gives the following conditions for the separation of tungsten from  $\text{WF}_6$  in a hydrogen current:

Temperature	200 to 800°C
Pressure	Vacuum up to a few atmospheres
H <sub>2</sub> :WF <sub>6</sub>	5:1 to 20:1

Flow velocity of the  
gas mixture

31 to 15.5 ml/min·cm<sup>2</sup>

In (Ref. 17) it is stated that at a ratio of  $H_2.WF_6 = 140$  and pressures of /10 20 Torr the separation of tungsten at 800°C is inhomegonous. At 600°C it was more uniform and at 500°C there was no more separation. Layers with the dimensions 8 x 1 1/4 x 0.06 inches were deposited on copper at 700°C and with  $WF_6$ - flow rates of 200 ml/min. The analysis resulted in (ppm):

C	18-50	N	<5-13
O	12-60	F	10-40
H	1-11	Cu	1-10

US-Patent 3,072,983 (Ref. 18) emphasizes the advantages of the reduction of  $WF_6$  with hydrogen over other methods of separation of tungsten layers. According to this,  $W(CO)_6$  is unsuitable for many applications as well as too expensive. The reduction of  $WCl_6$  with hydrogen becomes practical only at 850°C (a temperature at which layers adhere well and appreciable separation rates can be obtained). In contrast to this, the quality of the tungsten layers when  $WF_6$  is used in a hydrogen current is independent of temperature and pressure over large ranges. Even though the separation temperature depends on the properties of the material to be vaporized, a temperature of 650°C should be favorable in most cases. The following data are presented in the patent document:

Temperature Region	300 to 900°C
Pressure Range	0.1 to 100 atm
Total Amount of Flow	400 to 3600 ml/min
Substances on which tungsten was deposited	Graphite, Copper Steel and Molybdenum

The following conditions are given for the deposition of tungsten on molybdenum, steel and graphite:

1. Deposition on molybdenum  
650°C, 1 atm  
3200 ml  $H_2$ /min  
340 ml  $WF_6$ /min  
Duration: 30 min.  
Tungsten layer: 0.023 in.

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2. Deposition on a steel cylinder

650°C, 0.5 atm

200 ml H<sub>2</sub>/min

200 ml WF<sub>6</sub>/min

Duration: 30 min.

Deposited amount of tungsten: 7.5 g

3. Deposition on a graphite rod

650°C, 0.1 atm

1000 ml H<sub>2</sub>/min

345 ml WF<sub>6</sub>/min

Deposited amount of tungsten: 3.5 g

This paper does not contain sketches of the experimental apparatus.

Miller (Ref. 19) describes investigations of the deposition of especially pure tungsten on sapphire monocrystals by the reduction of WF<sub>6</sub> with hydrogen.

He gives the following separation conditions:

250°C,  $5.5 \cdot 10^{-2}$  to  $1.75 \cdot 10^{-1}$  Torr, H<sub>2</sub>:WF<sub>6</sub> = 1:1

Layer thickness 100 to 2700 Å/h

1000°C,  $2 \cdot 10^{-3}$  Torr, H<sub>2</sub>:WF<sub>6</sub> = 6:1

WCl<sub>6</sub>

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Steel-blue crystals; the vapor is weakly disassociated.

Flow point 275°C, Condensation point 347°C

Manufacture from the elements.

Oxley (Ref. 20) describes a method for depositing layers on uranium dioxide, in which WCl<sub>6</sub> is disassociated in a hydrogen current at 400°C (100 to 150-fold excess). The WCl<sub>6</sub> is vaporized, is carried to the reaction zone by an argon current, and is mixed with hydrogen there. The hydrogen chloride formed during the reaction is collected in subsequent washing and drying towers. The hydrogen is first freed of oxygen and is cleaned by means of a molecular sieve.

The amount of tungsten separated is about 0.6 g/h·cm<sup>2</sup> on the average. The chlorine content of the layer at 400°C is quite large (5000 to 1900 ppm), but the cohesion of the tungsten on the uranium dioxide is good.

According to Lamprey (Ref. 10) WCl<sub>6</sub> or MoCl<sub>5</sub>, respectively, are introduced into a reaction tube by means of an argon current in the manufacture of tungsten or molybdenum powder. They are then mixed with hydrogen and are decomposed at



temperatures between 450 and 900°C. The chlorine content of the separated metals varies between 1.82 weight % (430°C) and 0.13 weight % (905°C). The particle diameter was 0.01 to 0.1  $\mu\text{m}$ .

Finally, we would again like to mention US-Patent 3,089,785 (Ref. 11) in this connection.

### WBr<sub>6</sub>

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Blue-black, sublimating needles, which decompose with a small amount of heating.

Manufacture from the elements.

In the manufacture of tungsten bromide, WBr<sub>6</sub>, WBr<sub>5</sub>, WBr<sub>4</sub> and WBr<sub>3</sub> are created at the same time, which sublime above 230°C. According to Caves (Ref. 21), these bromides are vaporized at 108 to 386°C and are decomposed at temperatures between 1100 to 1540°C and pressures of 10<sup>-7</sup> Torr. Apparently very pure tungsten is separated using this modified van-Arkel-de-Boer method.

### Rhenium

Density 20.53 g/cm<sup>3</sup>

Flow point 3167 $\pm$ 60°C

Condensation point 5870°C (5630°C)

Further physical and chemical properties can be found in Schreiter (Ref. 4), Gosner (Ref. 22) and Lebedev (Ref. 23). For technical data see Sagoschen (Ref. 24). The pure metal is manufactured via ReCl<sub>5</sub>.

The initial materials for the manufacture of rhenium layers were ReF<sub>6</sub> and ReOCl<sub>4</sub>. (Re(CO)<sub>5</sub>)<sub>2</sub> is also a possibility.

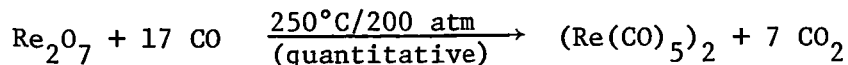
### (Re(CO)<sub>5</sub>)<sub>2</sub>

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Flow point 177°C, sublimates after 140°C

Above 177°C slow decomposition begins

Manufacture:



This compound is not used for the manufacture of coatings, as far as can be seen from the literature. Nevertheless we will mention the data, since they can be of interest.

ReF<sub>6</sub>

Pale yellow crystals

Flow point 25.6°C, Condensation point 47.6°C

Manufacture from the elements.

ReF<sub>6</sub> is very unstable. It reacts with water, fats, glass, quartz (already below 30°C), ligroin, etc. ReF<sub>6</sub> can be reduced by hydrogen, (above 200°C), with carbon monoxide (above 300°C), as well as with sulfur dioxide (above 400°C), where ReF<sub>4</sub> or metallic rhenium (at 400 to 500°C) is formed.

According to Federer (Ref. 25) rhenium is separated from ReF<sub>6</sub> in a hydrogen current (500 to 3000 ml/min) at temperatures between 400 to 800°C and pressures < 10 Torr in a uniform way. Even before the beginning of the decomposition process occurs, hydrogen (100 ml/min) is added to the ReF<sub>6</sub>, whose purpose is to protect the glass components, and in particular the flow meter, from corrosion.

Experiments on the manufacture of tungsten-rhenium alloys by Federer (Ref. 25) show that the composition of the layers depends on the decomposition temperature. Depending on the rhenium content, it is possible to work with a flow of 30 ml WF<sub>6</sub> and 2000 ml hydrogen per minute, in the temperature region between 500 to 700°C and at a pressure of 10 Torr. /15

In (Ref. 17) it is stated that the rhenium separation is uniform at temperatures of 400°C and pressures of 10 Torr and a hydrogen flow rate of 2000 ml/min. 500 to 800°C and a flow rate of 3000 ml/min were found to be less advantageous.

According to (Ref. 17) tungsten-rhenium alloys with 25% rhenium can be manufactured at 700°C, 10 Torr and in the presence of 70 mole hydrogen per mole of total fluoride (71 % WF<sub>6</sub> + 29 % ReF<sub>6</sub>).

ReOCl<sub>4</sub>

Dark brown in the solid and vaporous state

Flow point 29°C, Condensation point 223°C

Manufacture by oxidation of ReCl<sub>4</sub> at 150°C

Even though pure rhenium is manufactured with ReCl<sub>5</sub>, which can easily be cleaned, it was not possible to find any method of manufacturing coatings in the literature which started with this compound. Instead of it, oxychloride is preferred.

According to USSR-Patent 155,933 (Ref. 26) ReOCl<sub>4</sub> was reduced to rhenium using hydrogen at 800 to 1000°C with the formation of hydrogen chloride.

160 mg/cm<sup>2</sup>·h of rhenium were also separated at 1200 to 1300°C. This is 16 times as much as when ReCl<sub>5</sub> is used as the initial material. The rhenium yield comprises 50 to 60% of the theoretical amount. ReOCl<sub>4</sub> is stable up to 600°C. ReCl<sub>5</sub> decomposes already at 200°C into ReCl<sub>3</sub>, which is hard to volatilize. ReOCl<sub>4</sub> was manufactured by oxidation of ReCl<sub>5</sub> at 80 to 150°C.

#### REFERENCES

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1. Hodgman, C.S. et al. Handbook of Chemistry and Physics, 43rd edition, 1961-1962. Chemical Rubber Publishing Company, 1961.
2. Sidgwick, N.V. The Chemical Elements and their Compounds, Vol. II. Oxford, Clarendon Press, 1962.
3. Sherwood, E.M. Vapor Plating. MID-Atlantic Regional Meeting. American Electroplaters' Society, May 1, 1965. Plating Magazine, July 1, 1965.
4. Schreiter, W. Seltene Metalle, Bd. II (Rare Metals, Vol. II). VEB German Publishing House for Raw Material Industry, Leipzig, 1961.
5. Braun, H. Metallic Molybdenum, Part I: Non-Alloyed Molybdenum. Metall, 16, p. 646, 1962.
6. Lander, I.J., Germer, L.H. Plating of Mo, W, Cr by Thermal Decomposition of their Carbonyls. Metals Technology, T.P. 2259, 1947.
7. Breining, E.R., Whitacre, J.R. Use of Dioxane as a Solvent for Vapor Plating Molybdenum, Tungsten and Chromium from their Hexacarbonyls. A.P. 3,023,491 (March 1962).
8. Gadiyar, H.S., Balachandra, J. Vapor Phase Deposition of Molybdenum on Uranium Dioxide Particles using Fluidized Bed Technique. Trans. Indian Inst. Metals 15, p. 264, 1962. /17
9. Badiali, A., Kirshenbaum, N.W., Bakish, R. Preparation of Ultra Pure Molybdenum. Trans. AIME 227, p. 32, 1963.
10. Lamprey, H., Ripley, R.L. Ultrafine Tungsten and Molybdenum Powders. J. Electrochem. Soc. 109, p. 713, 1962.
11. Lewis, J.G., Ohlgren, H.A. Process of Manufacturing Nuclear Fuel. A.P. 3,089,785 (May 1963).
12. McGuire, J.C. Simple Experimental Techniques for Deposition of Tungsten from Tungsten Hexacarbonyl. Trans. Am. Nucl. Soc. 7, H. 2, p. 426, 1964.
13. Anonymous. Metallurgy of Molybdenum, Niobium and Molybdenum-Niobium Alloys -- A Literature Search. TID 3572. Especially see the citations: 361, 688, 709, 752, 762, 831, 853 to 855, 866, 868, 923, 984, 1016, 1097, 1596.
14. Nieberlein, V.A., Kenworthy, H. High-Purity Tungsten by Fluoride Reduction. US Dept. of the Interior, Bureau of Mines, Washington, 1959. Report of Investigations 5539.
15. Oxley, J.H., et al. Fluoride Tungsten. Trans. Am. Nucl. Soc. 7, H. 2, p. 426, 1964. /18
16. Nyce, A.C. et al. Applications and Properties of the Tungsten Cementation Process. Trans. Am. Nucl. Soc. 7, H. 2, p. 427, 1964.
17. Anonymous. Vapor-Deposited Materials. Nucleonics 23, H. 2, p. 88, 1965.
18. Brenner, A., et al. Vapor Deposition of Tungsten. A.P. 3,072 January 1963.
19. Miller, A., Barnett, G.D. Chemical Vapor Deposition of Tungsten at Low

- Pressure. J. Electrochem. Soc. 109, p. 973, 1962.
20. Oxley, J.H., et al. Coating Uranium Dioxide Powders with Metallic Tungsten. Ind. Engng. Chem. 51, H. 11, p. 1391, 1959.
  21. Caves, R.M. Tungsten Coating from the Thermal Decomposition of Tungsten Bromides. Trans. AIME 224, p. 267, April, 1962.
  22. Gonser, B.W. Rhenium. Elsevier Publishing Comp., Amsterdam, New York, 1962.
  23. Lebedev, K.B. The Chemistry of Rhenium. London, Butterworth, 1962.
  24. Sagoschen, J. Rhenium. Metall, 16, p. 1193, 1962.
  25. Federer, J.J., et al. Vapor Deposition of Tungsten-Rhenium Alloys. Trans. 19 Am. Nucl. Soc. 7, H. 2, p. 425, 1964.
  26. USSR Patent 155,933, March 1963. Verfahren zur Herstellung von Rhenium (Manufacturing Methods of Rhenium).

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